Clinoenstatite as an Exsolution Phase in Diopside

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MEMOIRS OF THE FACULTY OF SCIENCE, KYOTO UNIVERSITY, SERIES OF GEOL. & MINERAL.
VOL. XXXVII, No.2, pp. 173-180, December 20, 1970

Clinoenstatite as an Exsolution Phase in Diopside*

By

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(Received September 18, 1970)

Abstract

Clinoenstatite ($Wo_1\ En_{89}\ Fs_{10}$) was found as an exsolution phase in some diopside crystals in ultrabasic rocks from the Hidaka metamorphic belt, Hokkaido, Japan. It may have occurred submicroscopically as a metastable phase under the lattice distortion in the early stage of the process of exsolution. In the later stage, this metastable phase is likely to have grown to the broad exsolution lamellae parallel to *(100)* of host diopside, so that they can be easily observed under the microscope. As the result, this metastable phase may have been released from the lattice distortion, and has been converted into orthoenstatite as a stable phase.

Introduction

Clinoenstatite occurs in some stony meteorites, but its occurrence has rarely been reported in terrestrial rocks.

In our previous study (YAMAGUCHI and TOMITA, 1968), monoclinic bronzite ($En_{80}\ Fs_{20}$) was found as an exsolution phase in host terrestrial diopside.

ATLAS (1952) demonstrated, from an experimental study on the stability relation of $MgSiO_3$, that clinoenstatite was found to be a metastable low temperature phase formed during rapid cooling of protoenstatite. On the other hand, TURNER *et al.* (1960) converted orthoenstatite into clinoenstatite by shearing stress at 500°-800°C. Later, SCLAR *et al.* (1964) reported that clinoenstatite has a stability field at high pressure and low temperature. Yet, it is still uncertain whether clinoenstatite has a stability field or not.

Recently, authors found a number of clinoenstatites as exsolution phases in some diopsides in ultrabasic rocks from the Hidaka metamorphic belt in Hokkaido, Japan.

From a view point of the polymorphic transformation of enstatite as an exsolution phase in diopside, the stability of clinoenstatite will be referred.

Specimen description

Ultrabasic rocks in the Hidaka metamorphic belt in Hokkaido were described by

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* Read at the IMA and IAGOD Meeting '70 (Sept. 2, 1970 in Kyoto.)

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HUNAHASHI and HASHIMOTO (1951), KOMATSU and NOCHI (1966), and NOCHI and KOMATSU (1967). The specimens examined in the present investigation are the diopsides from Horoman and Pankenushi ultrabasic bodies.

The crystals are bright green in color to the naked eye, and *(100)* diallage partings are pooly developed. The diopside has exsolution lamellae parallel to *(100)* (Fig. 1). The chemical composition and optical properties of these diopside specimens are shown in *Table 1*, and *Fig. 2*.

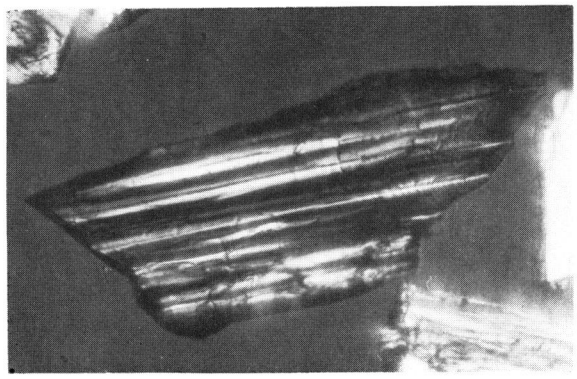

Fig. 1. *(100)* exsolution lamellae in diopside from Pankenushi. ×200

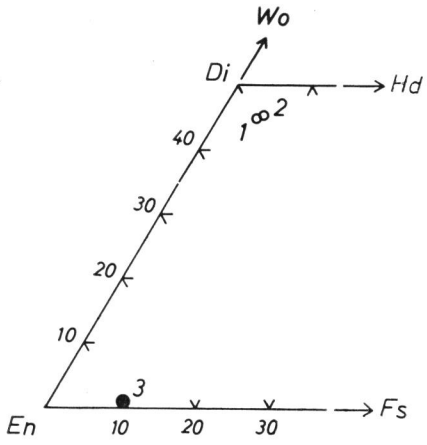

Fig. 2. Compositions of host diopsides and the exsolution lamellae plotted in diopside-hedenbergite-enstatite-ferrosilite diagram.

The chemical composition of the exsolution lamellae analysed by using electron probe microanalyser is also shown in *Table 1*. It has nearly identical composition to clinoenstatite phenocryst from Cape Vogel area, Papua (DALLWITZ *et al.* 1956).

Table 1. Chemical compositions and optical properties.

	1	2	3	4
SiO_2	51.91	51.45	54.39	
TiO_2	0.19	0.89		
Al_2O_3	4.59	4.02	3.50	
Cr_2O_3	0.61	0.82		
Fe_2O_3	1.19	1.42	FeO	
FeO	2.20	2.52	6.65	
MnO	0.15	n.d.		
MgO	17.07	16.67	33.17	
CaO	21.36	21.74	0.66	
Na_2O	n.d.	0.69		
K_2O	n.d.	0.00		
H_2O+	0.34	0.23		
H_2O-	0.08			
Total	99.69	100.45	98.37	
Mg	49.8	48.4	89	92~87
Fe	5.4	6.2	10	8~13
Ca	44.8	45.4	1	0
α				1.661~1.664
γ	1.700	1.701		
$2V_\gamma$	59°	60°		25°~56°
$C\wedge Z$	38°	41°	0~22°	28°~31°

1 ; Diopside from Horoman. Anal. Y. Yamaguchi.
2 ; Diopside from Pankenushi. Anal. M. Nochi.
3 ; *(100)* exsolution lamellae in diopside from Pankenushi. Anal. M. Komatsu.
4 ; Clinoenstatite phenocrysts from Cape Vogel area, Papua (Dallwitz et al. 1966).

Experimental

The *hkl*(k=0,1,2)* and *hkl* (l=0,1,2)* precession photographs were obtained on these diopside crystals by using Mo-kα radiation. The crystals from both Horoman and Pankenushi whose exsolution lamellae can be seen under the microscope display strong diffuse spots in X-ray diffraction photographs (Fig. 3). They are denoted by diopside *(H)* and diopside *(Pan 1)* respectively in this investigation. But, the small crystal from Pankenushi, in which no exsolution lamellae is detected under the microscope, does not show such strong diffuseness in diffraction spots (Fig. 4). It is denoted by diopside *(Pan 2)*.

In these precession photographs of the diopside crystals there appear extra spots by one or two exsolution phases besides those by host diopside phase (Fig. 3). They are arranged on the symmetrical positions related by the symmetry elements of the host diopside.

The lattice analysis was made on each photograph. From the examination of extinc-

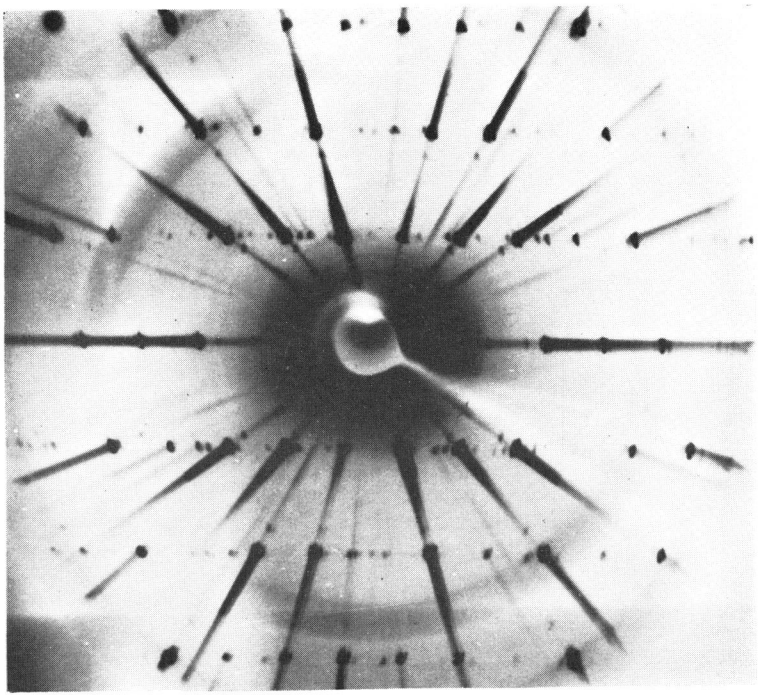

Fig. 3. *h0l* precession photograph of diopside crystal *(H)*.

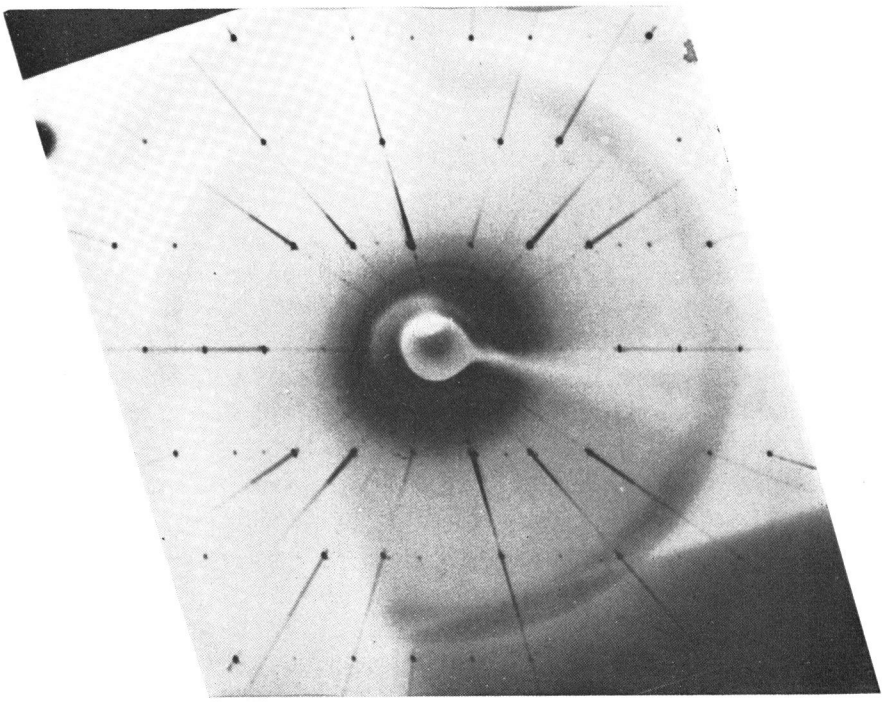

Fig. 4. *h0l* precession photograph of diopside crystal *(Pan 2)*.

tion rules on these extra spots, it is shown that one is monoclinic pyroxene whose space group is $P2_1/c$, and the other is orthorhombic pyroxene with space group *Pbca*.

Results of lattice analyses

Results of lattice analyses on exsolution phase in each crystal are represented as follows. The crystallographical relations of each crystalline phase and its lattice constants are shown in *Fig.* 5 and 6, and *Table 2* respectively.

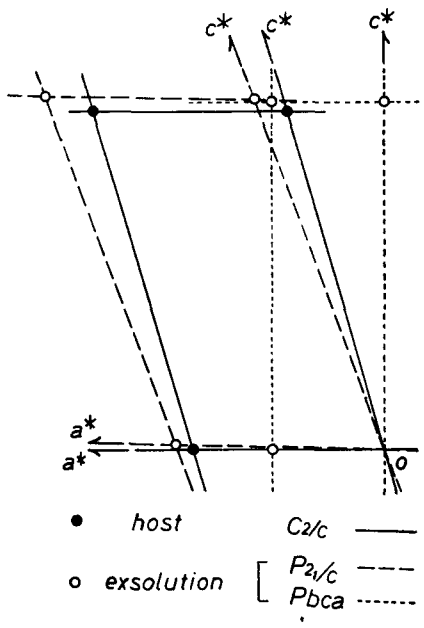

Fig. 5. *h0l* reciprocal plane of diopside crystal (H).

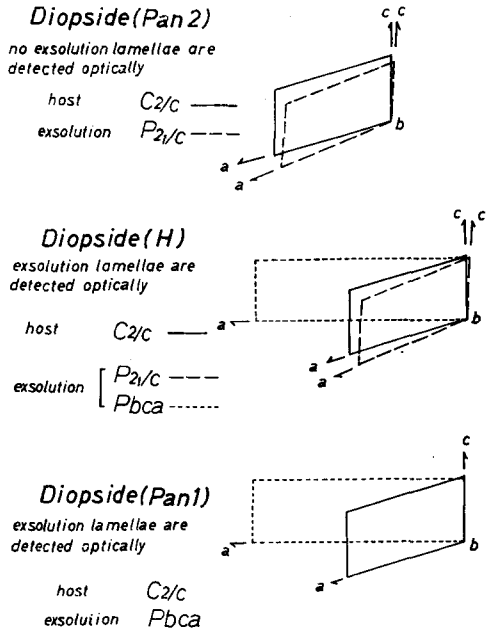

Fig. 6. Direct lattices of each diopside crystal.

The exsolved two phases and host diopside have common b^* axis in orientation, and a^* axes of the exsolved orthorhombic pyroxene and host diopside are common in orientation, while a^*axes of the exsolved monoclinic pyroxene and host diopside are slightly splitting in orientation.

Diopside (H) : It displays strong diffuse spots in the X-ray diffraction photographs, and the exsolution phases are composed of two different lattices, i.e., a monoclinic pyroxene with space group $P2_1/c$, and an orthorhombic pyroxene with space group *Pbca*.

Table 2. Lattice constants of the host diopsides and the exsolved phases.

		Horoman diopside crystal Exsolution lamellae can be seen under microscope *(diopside H)*	Pankenushi diopside crystal	
			No exsolution lamellae can be seen under microscope *(Pan 2)*	Exsolution lamellae can be seen under microscope *(Pan 1)*
exsolution	$P2_1/c$	$a=$ 9.59±0.01 Å $a\sin\beta=$ 9.09±0.01 Å $b=$ 8.82±0.01 Å $c=$ 5.20±0.01 Å $\beta=$ 108° 38′ ± 4′	$a=$ 9.59±0.01 Å $a\sin\beta=$ 9.09±0.01 Å $b=$ 8.88±0.01 Å $c=$ 5.18±0.01 Å $\beta=$ 108° 39′ ± 4′	
	Pbca	$a=$ 18.18±0.01 Å $b=$ 8.82±0.01 Å $c=$ 5.20±0.01 Å		$a=$ 18.18±0.01 Å $b=$ 8.83±0.01 Å $c=$ 5.20±0.01 Å
host	*C2/c*	$a=$ 9.717±0.001 Å $a\sin\beta=$ 9.335±0.001 Å $b=$ 8.889±0.001 Å $c=$ 5.250±0.001 Å $\beta=$ 106° 8′ ± 1′	$a=$ 9.72±0.01 Å $a\sin\beta=$ 9.34±0.01 Å $b=$ 8.89±0.01 Å $c=$ 5.25±0.01 Å $\beta=$ 106° 9′ ± 4′	

Diopside (Pan 1) : It displays also strong diffuse spots, and there is only an orthorhombic pyroxene with space group *Pbca* as an exsolution phase in addition to the host diopside phase.

Diopside (Pan 2) : Diffuseness in diffraction spots in X-ray photographs is extremely weak. Although the crystal is optically homogeneous under the microscope, extra spots are observed in addition to those of host diopside phase. There appears the existence of an exsolved phase of only a monoclinic pyroxene with space group $P2_1/c$. This exsolved monoclinic pyroxene in diopside *(Pan 2)* has slightly larger lattice constant b and slightly smaller lattice constant c than those of exsolved monoclinic pyroxene in diopside *(H)* respectively.

Discussion

Hitherto, majority of the studies on exsolution phenomena in pyroxene have been made on such specimens whose exsolution lamellae or blebs can be seen under the microscope (HESS 1941, HENRY 1942, POLDERVAART and HESS 1951, BROWN 1957). On the other hand, BOWN and Gay (1960) reported the detection of exsolution of pigeonite by an X-ray method in some augite cyrstals which are microscopically homogeneous.

In the present study, diopside crystal *(Pan 2)* is optically homogeneous under the microscope, but it has an exsolution phase of only a clinoenstatite in submicroscopical

domain size. On the other hand, the broad exsolution lamellae which can be easily observed under microscope in diopside crystals *(H)* and *(Pan 1)* are composed of either both orthoenstatite and clinoenstatite, or only orthoenstatite. This is the first description of clinoenstatite as an exsolution phase in pyroxene crystal.

It is worthy of notice, that the clinoenstatite in diopside crystal *(Pan 2)* is slightly different from that in diopside crystal *(H)* in lattice constant *b* and *c*.

Provided that two kinds of exsolved clinoenstatite have similar chemical composition, the difference in the lattice constants may be attributed to the lattice distortion caused at the time of the exsolution. The lattice distortion may be originated from the maintenance of a certain crystallographical relation not only in orientation but also in lattice constant between the host phases and the exsolved ones.

Judging from the points as described below, the exsolved clinoenstatite with a submicroscopic domain size in diopside crystal *(Pan 2)* may have undergone its lattice distortion.

1. Its lattice constant *b* presents close similarity to that of host diopside (Table 2), and therefore it does not exhibits the intrinsic lattice constants corresponding to its chemical composition (Table 3).

Table 3. Lattice constants of some clinoenstatite

Occurrence	Composition (metal ion)	*a*(Å)	*b*(Å)	*c*(Å)	*β*
1 Synthetic	Mg_{100}	9.618	8.825	5.186	108°21′
2 Synthetic	Mg_{100}	9.612	8.820	5.201	108°10′
3 Phenocryst from Papua	$Mg_{90}Fe_{10}$	9.61	8.82	5.18	108.4°
4 Exsolution in in diopside *(H)*	$Ca_1Mg_{89}Fe_{10}$	9.59	8.82	5.20	108°38′
5 Exsolution in diopside *(Pan 2)*		9.59	8.82	5.18	108°39′

1. Kuno and Hess (1953). 2. Lindemann (1956). 3. Morimoto et al. (1969).
4. This work. 5. This work.

2. The lattice distortion of exsolved phase may be presumably originated in the early stage in which the nucleation of exsolution phase has been submicroscopically progressing in host crystalline phase during the process of exsolution.

Therefore, clinoenstatite as an exsolution phase in diopside crystal *(Pan 2)* is regarded as a metastable phase which occurred under the lattice distortion in the early stage in the process of exsolution of enstatite from the host diopside. In the later stage, this metastable phase has grown to the borad lamellae parallel to *(100)* of host diopside, so that they can be easily observed under the microscope. As the result, its

lattice distortion was released, and the metastable clinoenstatite was converted into orthoenstatite as a stable phase.

Diffuseness in diffraction spots of the crystals which have the broad exsolution lamellae formed in the later stage may be considered to be an asterism as the result of this release from the lattice distortion.

Acknowledgments

Specimens used in this work were kindly supplied by Mr. M. KOMATSU, Hokkaido University, and Mr. NOCHI, The Civil Engineering Research Institute of Hokkaido Development Bureau. Mr. M. KOMATSU kindly analysed the chemical composition of the exsolution lamellae by using EPMA. The authors are very grateful to these persons. They also thank to Dr. K. YAGI, Professor of the Hokkaido University, for his great interest in this work and for his critical reading of the manuscript, and to Dr. T. UEDA, Assistant Professor of Kyoto University, for his giving them useful advice and for his critical reading of the manuscript.

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